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The Relative Coordinating Ability of Some Weak O-Donor Anions and Water Towards the $[Pt(terpy)]^{2+}$ (terpy = 2,2′:6′,2′′-terpyridine) Center – X-ray Crystal Structures of $[Pt(terpy)(H_2O)](CF_3SO_3)_2$ and $[Pt_2(\mu\text{-}OH)(terpy)_2](PF_6)_2(CF_3SO_3)$

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Acidolysis of the complexes $[Pt(CH_3)(terpy)]Y$ (Y = PF_6, CH_3SO_3, CF_3SO_3, ClO_4, BF_4; terpy = 2,2′:6′,2′′-terpyridine) with an equimolar amount of CH_3SO_3 in 2,2,2-trifluoroethanol (TFE) affords the corresponding methanesulfonato derivatives $[Pt(OSO_2CH_3)(terpy)]Y$. When Y = NO_3 a nearly equimolar mixture of the methanesulfonato and nitrato complexes is obtained, whereas the reaction of $[Pt(CH_3)(terpy)](CF_3SO_3)$ with triflic acid in either dry TFE or CH_2Cl_2 gives the aqua species $[Pt(terpy)(H_2O)](SO_3CF_3)_2$ (**8′**), whose X-ray crystal structure is reported. This structure shows hydrogen bonding between the coordinated water molecule and two triflate ions. ^1H NMR evidence is reported that suggests that this hydrogen bonding is partially retained in CD_3NO_2 solution. The new hydroxido-bridged dimers $[Pt_2(\mu\text{-}OH)(terpy)_2](X)$ [X = $(ClO_4)_3$, $(PF_6)_2(CF_3SO_3)$ (**12**)] have been isolated and their X-ray crystal structures determined.
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Introduction

Complexes of the transition metals containing weakly bonded anions (e.g. BF_4^-, $CF_3SO_3^-$, etc.) are of great importance in coordination and organometallic chemistry as they can serve as useful precursors for the preparation of a wide range of complexes, many of which have been shown to be active catalysts.[1] Some of the various routes used for their preparation have been reviewed by Beck.[2] Among these synthetic methods, the acidolysis of a metal–alkyl bond is of particular utility since it gives no by-products. We have successfully applied this route for the preparation of $[Pt(OSO_2CF_3)(triphos)](CF_3SO_3)$ {triphos = bis[2-(diphenylphosphanyl)ethyl](phenyl)phosphane} by treating $[Pt(CH_3)(triphos)](CF_3SO_3)$[3] or $[Pt(CH_3)_2(triphos\text{-}P,P')]$[4] with CF_3SO_3H. Both these reactions give the triflato complex cleanly and in high yield.

We reasoned that acidolysis of a cationic complex of the type $[M(CH_3)(L)]Y$ (L = terdentate ligand) with an acid HY′ could also be useful for establishing the relative coordinating ability of the two anions Y and Y′. We chose 2,2′:6,2′′-terpyridine (terpy) as the terdentate ligand to take advantage of our own experience in the chemistry of Pt^{II},[5–7] and Au^{III}(terpy)[8] complexes as well as of the impressive amount of existing literature data, particularly papers by Romeo et al. dealing with the $[Pt(CH_3)(terpy)]^+$ cation.[9–11]

It is well known that a terpy ligand gives rise to extensive charge delocalization in an expanded π system when coordinated to a metal ion.[12,13] This results in a remarkable increase in the electrophilicity of the metal center, and we expected that this would favor the interaction with hard ligands such those we were dealing with here.

Herein we report the results of the acidolysis of the complexes $[Pt(CH_3)(terpy)]Y$ (Y = PF_6, CH_3SO_3, CF_3SO_3, ClO_4, BF_4, NO_3) by CH_3SO_3H and CF_3SO_3H (Y = CF_3SO_3). The crystal and molecular structures of the aqua species $[Pt(terpy)(H_2O)](CF_3SO_3)_2$ and of $[Pt_2(\mu\text{-}OH)(terpy)_2](PF_6)_2(CF_3SO_3)$, which have been isolated in the course of this work, are also reported.

Results and Discussion

Some of the starting complexes of the type $[Pt(CH_3)(terpy)]Y$ were prepared as described by Romeo et al.,[9] whereas the others (Y = NO_3, BF_4, CH_3SO_3 and CF_3SO_3) were obtained by treating $[Pt(CH_3)(terpy)](Cl)$ with a stoichiometric amount of the appropriate silver salt. All of them were dried under vacuum at 100 °C over P_2O_5 for at least 2 h before treatment with the acid.

Reactions of the Methyl Complexes with CH_3SO_3H

The reactions between equimolar quantities of the methyl complexes $[Pt(CH_3)(terpy)]Y$ [Y = PF_6 (**2**), ClO_4 (**3**),

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CF_3SO_3 (**4**), BF_4 (**5**), NO_3 (**6**), CH_3SO_3 (**7**)] and CH_3SO_3H proceed readily in 2,2,2-trifluoroethanol (TFE) solution (room temp., 1 h) to yield the corresponding acidolysis products **2′**–**7′** in 80–90% yield (see Experimental Section). All complexes were characterized by microanalysis and ^1H NMR and IR spectroscopy.

The CH_3SO_3 resonance in the ^1H NMR spectra (CD_3NO_2) of complexes [Pt(OSO_2CH_3)(terpy)]Y (**2′**–**5′**) appears as a singlet at δ = 3.11 ppm, which is 0.64 ppm downfield from that observed in the methanesulfonate salt **7**. Resonances for both the coordinated and ionic methanesulfonate are present in the spectrum of complex **7′** in a 1:1 ratio. Hence, exchange between these two species, if any, is slow on the NMR timescale. Complexes **2′**, **3′**, **4′**, **5′**, and **7′** display the same spectrum, which is characterized by three groups of lines, in the aromatic region (terpy ligand). The most downfield-shifted signal at δ = 8.86 ppm, attributable to H^6, is a doublet coupled with H^5 ($^3J_{H,H}$ = 5.6 Hz) with satellite peaks due to ^{195}Pt coupling ($^3J_{Pt,H}$ = 32 Hz). The signal at δ = 7.98 ppm is a doublet of doublets assignable to H^5 ($^3J_{H,H}$ = 5.6 and 7.5 Hz; $^4J_{H,H}$ = 2.0 Hz). The remaining multiplets at δ = 8.59–8.34 ppm belong to the other aromatic ring protons. On the whole, the pattern here is very similar to that of the corresponding methyl complexes.

IR spectroscopy confirmed the identity of the complexes also in the solid state. This was best proved by comparing the spectrum of the methanesulfonate complex salt **7** with that of **2′**, whose PF_6^- counterion, which absorbs at 848 cm^{-1}, is transparent across the whole $\nu(SO_3)$ region (1000–1300 cm^{-1}). Thus, while **7** exhibits two strong absorptions at 1193 and 1038 cm^{-1}, which are typical values for the $\nu(SO_3)$ mode in ionic sulfonates, **2′** shows three peaks at 1275, 1150, and 1100 cm^{-1}. This increase in the multiplicity is typical of methanesulfonato complexes and is a consequence of a lowering of the symmetry of the SO_3 group upon coordination.[14] The analytical data for the acidolysis reaction product when Y = NO_3 (**6′**) are in keeping with the molecular formulation [Pt(terpy)(CH_3SO_3)(NO_3)]. The IR spectrum of the compound in the range 1300–1000 cm^{-1} is somewhat complex due to the overlapping of similar vibration bands for the NO_3 and SO_3 groups. However, bands arising from both ionic and coordinated anions appear to be present. Thus, the strong absorptions at 1519 and 1350 cm^{-1} can be assigned to coordinated and ionic NO_3^-, respectively, and those at 1275 and 1150 cm^{-1} to covalent methanesulfonate, while the two bands at 1203 and 1045 cm^{-1} are characteristic absorptions of ionic $CH_3SO_3^-$.

The ^1H NMR spectrum (CD_3NO_2) of **6′** displays two singlets in a 1:1 ratio at δ = 3.11 and 2.47 ppm due to coordinated and ionic $CH_3SO_3^-$, respectively. The aromatic region is characterized by peaks characteristic of the species [Pt(OSO_2CH_3)(terpy)]$^+$ and other resonances which, in view of the above findings, can be attributed to the terpy ligand in the cation [Pt(ONO_2)(terpy)]$^+$. In particular, the doublet at δ = 8.58 ppm, which is not present in the ^1H NMR spectra of the methanesulfonato complexes, is attributable to the H^6 terpy protons of [Pt(ONO_2)(terpy)]$^+$. We conclude from these observations that the acidolysis product **6′** is actually a nearly equimolar mixture of the methanesulfonato and nitrato complex salts. This, in turn, indicates that the two anions are of nearly equal coordinating ability toward the Pt(terpy) center, as is found for their basicity towards the proton.[15]

The acidolysis reactions of complexes **2**, **3**, **4**, and **7** with a stoichiometric amount of acid were monitored by ^1H NMR spectroscopy for CD_3NO_2 solutions (0.02 mmol of complex in 1 mL of CD_3NO_2). With the exception of complex **7**, all reactions went to completion in the time required for mixing the reagents. Surprisingly enough, **7** reacts with the acid very much more slowly: even at 40 °C it takes more than one week to go to about 90% conversion. Only the starting and final products are observed in the NMR spectra at any one time. A possible explanation for the above finding may be the formation of a hydrogen-bonded couple between the acid and its conjugate base in CD_3NO_2 solution, perhaps similar to that found between HNO_3 and NO_3^-,[16] in other words [$CH_3O_2SO\cdots H\cdots OSO_2CH_3$]$^-$. Such an interaction is unlikely to exist in the protic solvent TFE, which is why there is no difference in reactivity between **7** and the other methyl complexes.

Reactions of 4 with CF_3SO_3H

The reaction of [Pt(terpy)(CH_3)](CF_3SO_3) with a stoichiometric amount of triflic acid in either TFE or CH_2Cl_2 gives a compound (**8′**) whose analytical data indicate the presence of water, which was not lost on heating the compound at 100 °C under vacuum over P_2O_5 for several hours. Repeated and careful attempts to rigorously exclude water during the preparations failed. Since the IR and NMR spectroscopic data were not conclusive, an X-ray diffraction structural study of the compound was deemed necessary. This showed the compound is actually the aqua species [Pt(terpy)(OH_2)](CF_3SO_3)$_2$. This was a rather unexpected result, especially for the reaction conducted in CH_2Cl_2 since, as mentioned in the Introduction, we have previously found the same procedure to give the triflato complexes in the triphos and triphos-*P*,*P′* cases.

Structure of [Pt(terpy)(H_2O)](CF_3SO_3)$_2$ (8′)

An ORTEP[17] view of [Pt(terpy)(H_2O)](CF_3SO_3)$_2$ (**8′**) is shown in Figure 1. The coordination geometry around the platinum atom is distorted square-planar due to the constraints of the terpyridine ligand, which gives rise to a narrowing of N–Pt–N(*cis*) angles to 81.4(2)° and 81.8(2)°. These distortions are associated with a significant shortening of the Pt–N2 distance [1.914(4) Å] with respect to the Pt–N1 and Pt–N3 ones [2.021(5) and 2.009(4) Å, respectively], in agreement with the geometries observed in similar complexes of Pt^{II} with ter- or tetradentate ligands.[18–23] The three coordinated terpy nitrogen atoms, the platinum atom, and the water oxygen atom lie approximately in the same plane with maximum deviations from this plane for O1 of 0.033(5) Å and for N2 of 0.025(5) Å. The water molecule is located in a plane nearly perpendicular [84(5)°] to the Pt1

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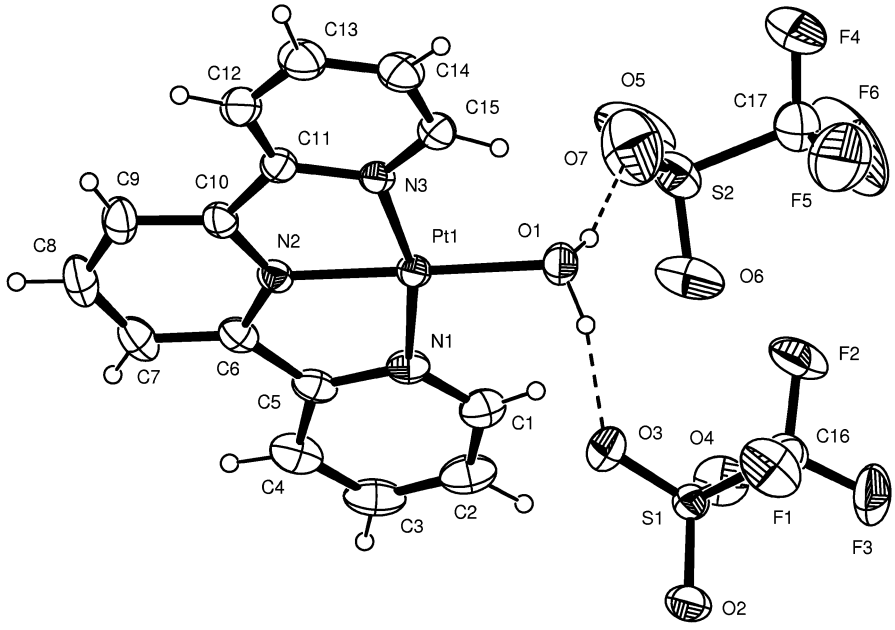

Figure 1. ORTEP view of $[Pt(terpy)(H_2O)](CF_3SO_3)_2$ displaying thermal ellipsoids at 30% probability. The dotted lines indicate hydrogen bonds.

basal plane and is linked to the oxygen atoms of two triflate anions by hydrogen bonds. The Pt–OH_2 distance [2.040(5) Å] compares well with the distances observed in Pt^{II} square-planar complexes where a water molecule is *trans* to a nitrogen atom (range: 2.05–2.10 Å).[24] No stacking interactions between parallel molecular planes shorter than the sum of the van der Waals radii are observed.

IR and ^{1}H NMR Spectroscopic Studies of the Aqua Complex $[Pt(terpy)(H_2O)](CF_3SO_3)_2$ (8′)

The IR spectrum of complex **8′** shows three strong absorptions in the $\nu(SO_3)$ region at 1166, 1235, and 1290 cm^{-1}. In light of the structural results, this increase in multiplicity of the $\nu(SO_3)$ mode can now be straightforwardly ascribed to the lowering of the symmetry of the SO_3 group due to hydrogen bonding with the coordinated water molecule. It should be noted that an increase in multiplicity would also be expected if the triflate ion were coordinated to the metal center, although the splitting here is somewhat smaller than in the triphos and triphos-*P,P′* triflate complexes.[3,4]

We isolated the aqua complex as its perchlorate salt $[Pt(terpy)(H_2O)](ClO_4)_2$ (**10**) after treating the corresponding salt of the methyl complex with an excess of perchloric acid in TFE. The ^{1}H NMR spectra of complexes **8′** and **10** in CD_3NO_2 solution are shown in Figure 2 (**8′**: spectrum A; **10**: spectrum C). In contrast to spectrum C, there are two doublets in the terpy-H^6 region of spectrum A, at δ = 8.76 and 8.67 ppm, both with a $^3J_{H,H}$ coupling constant of 5.6 Hz. Addition of lithium triflate to the solution of **10** causes an increase of the doublet at δ = 8.67 ppm and a corresponding decrease of the one at δ = 8.76 ppm (Figure 2, spectrum B).

The following further observations were made:
(i) The ^{1}H spectrum of $[Pt(H_2O)(terpy)](SO_3CF_3)_2$ (**8′**) after saturation of the CD_3NO_2 solution with $LiClO_4$ becomes identical to that of the perchlorate derivative **10**.
(ii) The addition of increasing amounts of lithium triflate to the solution of **8′** causes an increase of the upfield doublet and a corresponding decrease in the downfield one. However, even on saturating the solution with the triflate salt, the downfield doublet can still be observed.

Among the possible explanations we considered for the above results, we can definitively rule out the formation of ion pairs (without hydrogen bonding) and/or dimerization/oligomerization through stacking interactions, which are known to affect the NMR spectra of some Pt(terpyridine) complexes.[9] We have never found evidence for stacking in nitromethane solutions for either monocationic methyl or methanesulfonato complexes. Moreover, this should be even more disfavored for a dicationic species such as the aqua complex. The ^{1}H NMR spectrum of the similarly charged species $[Pt(CH_3CN)(terpy)]^{2+}$, which we have isolated as the triflate salt (see Experimental Section), does not show any tendency to undergo ion pairing in CD_3NO_2 solution.

A more likely explanation for the NMR spectra of derivatives **8′** and **10** and their behavior towards salt addition, which is supported by the X-ray data of **8′**, is the presence of a slow (on the NMR timescale) equilibrium between the $[Pt(terpy)(H_2O)]^{2+}$ species and a hydrogen-bonded adduct of the type $[Pt(terpy)(OH_2\cdots OSO_2CF_3)]^+$, this latter having the H^6 doublet at δ = 8.67 ppm in CD_3NO_2 solution. The addition of increasing amounts of lithium triflate to the solution, besides having the obvious effect of shifting the equilibrium towards the hydrogen-bonded adduct, also increases the ionic strength of the solution, which has the

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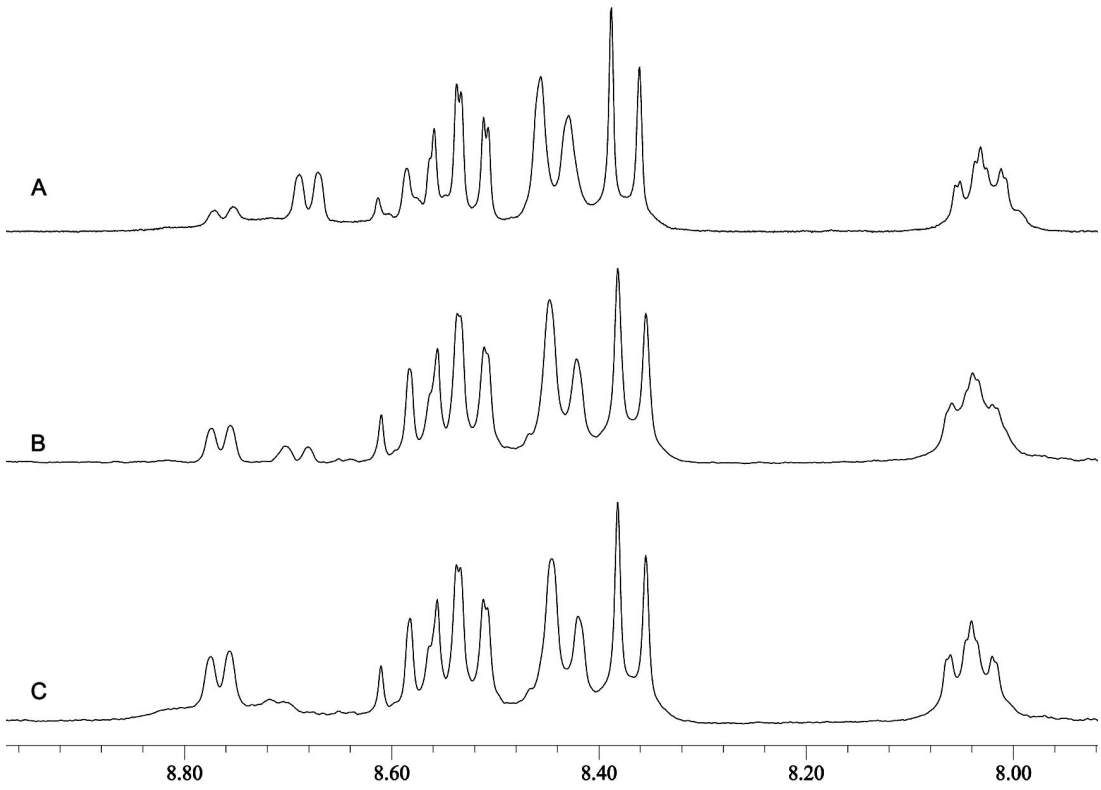

Figure 2. ^{1}H NMR spectra (δ values in ppm) of [Pt(terpy)(H_2O)](SO_3CF_3)$_2$ (A), [Pt(terpy)(H_2O)](ClO_4)$_2$ + 1/2 equiv. $LiSO_3CF_3$ (B) and pure [Pt(terpy)(H_2O)](ClO_4)$_2$ (C) in CD_3NO_2 at 298 K.

opposite effect. This explains why we still observe the downfield doublet even in solutions saturated with the triflate salt. The perchlorate ion, on the contrary, has a much lower (if any) hydrogen-bond-acceptor ability than triflate: It only increases the ionic strength and, when added in large amounts, completely shifts the equilibrium towards the $[Pt(terpy)(H_2O)]^{2+}$ species.

Some years ago, Lawrence et al. reported the isolation of a triflato complex after treating [PtCl(terpy)](Cl) with anhydrous CF_3SO_3H which, on the basis of the analytical data, they formulated as [Pt(OSO_2CF_3)(terpy)](CF_3SO_3)·CF_3SO_3H.[25] Unfortunately, the authors did not report IR or NMR spectroscopic data for their compound and, in our hands, attempts to follow their procedure always resulted in the isolation of intractable materials. As an alternative possible route to the synthesis of the triflato complex, we treated the methoxido complex [Pt(terpy)(OCH_3)](CF_3SO_3) (**9**) with an excess of methyl triflate in CH_2Cl_2, as described in the Experimental Section. The following reaction was expected to occur: [Pt(terpy)(OCH_3)](CF_3SO_3) + $CF_3SO_2OCH_3$ → [Pt(OSO_2CF_3)(terpy)](CF_3SO_3) + $(CH_3)_2O$.

The IR spectrum of the isolated product (**12**) shows three strong absorptions in the $\nu(SO_3)$ region at 1167, 1248, and 1297 cm^{-1}, while that observed at 848 cm^{-1} is typical of ionic PF_6. In the ^{1}H NMR spectrum (CD_3NO_2), the resonance of the H^6 proton of the terpy ligand is a doublet at δ = 9.43 ($^3J_{H,H}$ = 5.0 Hz) ppm. Once again, an X-ray diffraction structural study was necessary to unequivocally establish the identity of the compound as [Pt_2(μ-OH)(terpy)$_2$](PF_6)$_2$(CF_3SO_3).

Structure of [Pt$_2$(μ-OH)(terpy)$_2$](PF$_6$)$_2$(CF$_3$SO$_3$) (12)

An ORTEP view of the $[Pt_2(\mu\text{-OH})(terpy)_2]^{3+}$·($CF_3SO_3$) fragment is shown in Figure 2. The coordination geometry around both platinum atoms is distorted square-planar, and the geometrical parameters around each Pt atom are similar to those observed in complex **8′**, with the N–Pt–N(*cis*) angles within the range 81.0(3)–82.1(3)° and central Pt1–N2 and Pt2–N5 bond lengths of 1.906(7) and 1.917(7) Å, respectively. The coordination planes including the Pt atoms make angles of 56.3(5)° and 53.2(4)° with the plane of the Pt1–O1–Pt2 bridge and are almost perpendicular to each other, being rotated by an angle of 79.1(2)°. The Pt–O distances between the platinum atoms and the negatively charged bridging hydroxido group [2.033(6) and 2.024(6) Å] are slightly shorter than the Pt–O(water) distances (2.04–2.10 Å) observed in the previous structure (**8′**) and in square-planar Pt^{II} complexes where a water molecule is *trans* to a nitrogen atom.[24] The hydroxido group is hydrogen-bonded to the disordered triflate anion with an O1···O2 distance of 2.656(15) Å (Figure 3).

Interestingly enough, the same hydroxido-bridged dimer is obtained as its perchlorate salt [Pt_2(μ-OH)(terpy)$_2$](ClO_4)$_3$ (**11**) upon treating the methyl precursor with an excess of $HClO_4$ in water. We can draw this conclusion on the

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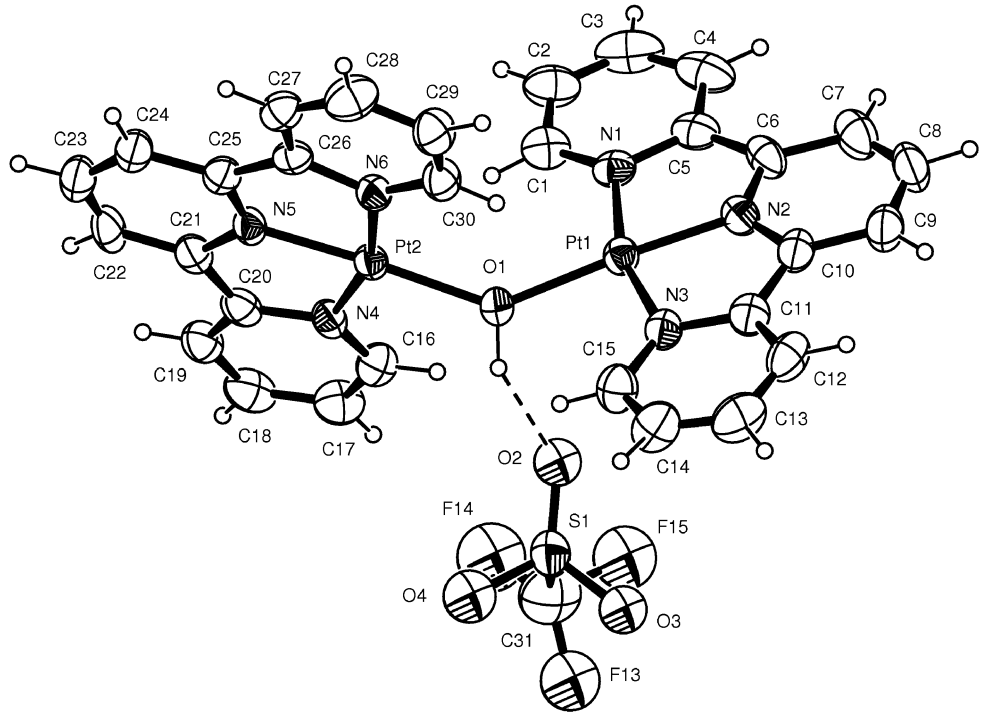

Figure 3. ORTEP view of the $[Pt_2(\mu\text{-}OH)(terpy)_2]^{3+}\cdot(CF_3SO_3)$ fragment displaying thermal ellipsoids at 30% probability. The dotted lines indicate hydrogen bonds.

basis of the analytical data and on the observation that the ^1H NMR spectra (CD_3NO_2) of the triflate hexafluorophosphate and perchlorate salts are identical. This latter result also indicates that, contrary to the case of the aqua species, the hydrogen bonding that is found in the solid state is not retained to any detectable extent in nitromethane solution.

Conclusions

The Pt^{II}(terpy) system behaves differently from the triphos and triphos-*P*,*P*′ ones in that only the aqua species, instead of the triflato complex, is isolated after the acidolysis of $[Pt(terpy)(CH_3)]^+$ under similar experimental conditions. It has been shown that the terpy ligand remarkably enhances the reactivity toward nucleophilic substitution when coordinated to a metal ion[7,26] and, moreover, that the triflate ion is a very weak ligand. On these grounds, the possibility exists that the first formed product of the acidolysis reaction is the triflato species, which then rapidly solvolyses to the aqua species. Given that water was only adventitiously present in the solvents we used, the rate constant for the solvolysis has to be quite high indeed. Lawrence et al. have reported a value of 0.1 s^{-1} for the rate constant of aquation of the triflato species they isolated in 0.1 M CF_3SO_3H.[25] On the other hand, since we have reported a value of 2.24×10^{-2} s^{-1} for the aquation of the $[Pt(terpy)Cl]^+$ species,[27] these two data would indicate a surprisingly low value of about 5 as the ratio of triflate/chloride lability. If so, aquation by adventitious water will be so slow that it is not likely to account for our experimental results. Considering the many examples of the unusual chemistry of (terpy)metal compounds reported in the literature, it might be possible that the mechanism of Pt–C bond fission is, in our case, different from that of the triphos and triphos-*P*,*P*′ ones. For example, it might be that it is not the bare proton that reacts to directly give the aqua species but the hydroxonium triflate instead. Some kinetic work is necessary, however, before any definitive conclusion can be drawn.

The isolation of $[Pt_2(\mu\text{-}OH)(terpy)_2](PF_6)_2(CF_3SO_3)$ (**12**) and its perchlorate analogue **11** is a rather noteworthy result and, although we did not pursue our investigation of the chemistry of these species further, a few considerations can nevertheless be made. First of all, species **11** can be isolated simply by changing the solvent from TFE, where the aqua species forms, to water. It might be reasoned that this is due to some reaction involving $[Pt(OH)(terpy)]^+$, which is formed by acid dissociation of the aqua species. This possibility can, however, be ruled out since any dissociation of the aqua species (pK_a = 4.4)[26] is completely suppressed under our conditions (excess $HClO_4$). It is much more likely that, since extensive dimerization of the reactive $[Pt(CH_3)(terpy)]^+$ species occurs in water, whereas in solvents such as TFE it does not,[9] the dimers are the actual reactive species. All in all, this result further demonstrates, in a striking way, the preference of the Pt(terpy) center for water instead of the triflate ion.

Finally, it is interesting to note that the molecular structures of **8**′ and **12** can be considered as being derived from the structure of the triflic acid monohydrate[28] by replacing one or two CF_3SO_3H molecules, respectively, with a

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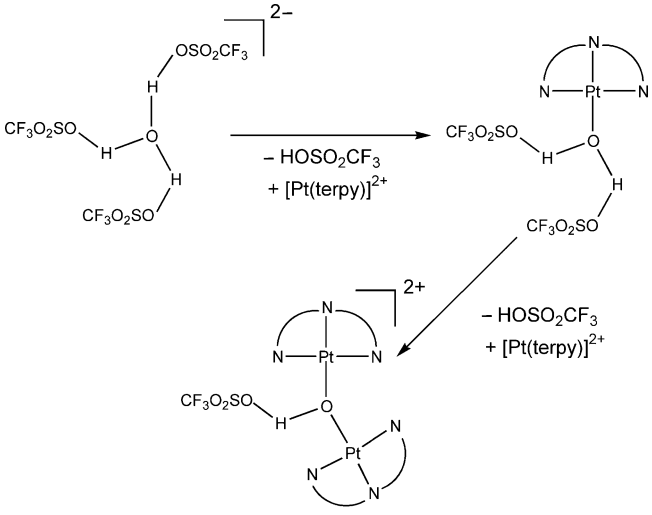
[Pt(terpy)]$^{2+}$ moiety, as depicted below (see Scheme 1). As such, this demonstrates once more the remarkable electrophilicity of the metal center caused by the terpyridine ligand.

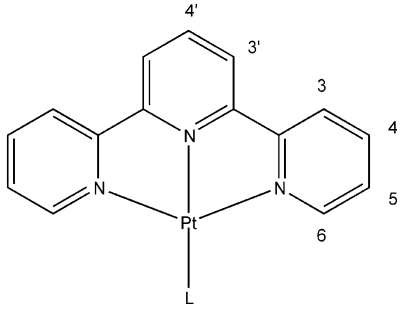


Scheme 1. Formal equivalence of the [Pt(terpy)]$^{2+}$ and $HOSO_2CF_3$ fragments in the monohydrate triflic acid, [Pt(terpy)(H_2O)]-(OSO_2CF_3)$_2$, and [Pt$_2$(μ-OH···OSO_2CF_3)(terpy)$_2$]$^{2+}$ crystal structures.

Experimental Section

Materials: 2,2,2-Trifluoroethanol (TFE, 99% from Aldrich) was treated with a quantity of sodium calculated for a 2% water content and then distilled under dry nitrogen. The other solvents used were purified and dried by standard techniques. 2,2′:6′,2′′-Terpyridine and inorganic salts were purchased from Aldrich. Pt^{II} precursors were prepared from platinum foils. Perchloric acid solution (65% in H_2O), methanesulfonic acid (>99.5%), triflic acid (>99%), and methyl methanesulfonate (>99%) were best-quality Aldrich products.

Instrumentation: IR spectra were recorded for nujol mulls between NaCl plates with a Nicolet Magna FT IR 750 or a Perkin–Elmer Spectrum One spectrometer. ^{1}H NMR spectra were recorded with a Bruker Avance 300 or Bruker AC 200 F spectrometer. Chemical shifts (ppm) were referenced internally to the undeuterated solvent resonances and are quoted relative to tetramethylsilane (δ = 0 ppm). The protons of the terpy ligand are numbered as in Scheme 2. Elemental analyses were performed by the Microanalytical Laboratory of the University at Padua.



Scheme 2. Numbering of the hydrogen and primary carbon atoms of the coordinated terpy ligand.

Preparation of the Complexes: The complexes [Pt(CH_3)(terpy)]Y [Y = Cl (**1**), PF_6 (**2**), ClO_4 (**3**), and CF_3SO_3 (**4**)] were prepared according to reported procedures.[9] Their chemical analyses are in good agreement with those obtained in previous preparations. The analogous BF_4 (**5**), NO_3 (**6**), and CH_3SO_3 (**7**) salts were prepared by treating the chlorido complex **1** (typically 0.1 g, 0.21 mmol) with a stoichiometric amount of the appropriate silver salt in water (approx. 15 mL). After stirring the mixture in the dark at room temperature for about 1 h, the AgCl was filtered off and the solvent completely removed under vacuum. The crude products were recrystallized from a TFE/diethyl ether mixture. In every case the yield was practically quantitative. **5:** $C_{16}H_{14}BF_4N_3Pt$ (530.19): calcd. C 36.2, H 2.66, N 7.93; found C 36.3, H 2.70, N 7.91. **6:** $C_{16}H_{14}N_4O_3Pt$ (505.39): calcd. C 38.0, H 2.79, N 11.1; found C 38.2, H 2.82, N 11.0. ^{1}H NMR (**5**, **6**; CD_3NO_2): δ = 8.81 (d, $^3J_{H,H}$ = 5.9, $^3J_{Pt,H}$ = 51 Hz, 2 H, H^6), 8.53–8.25 (m, 7 H, H^4, H^3, H$^{3'}$, H$^{4'}$), 7.78 (ddd, $^3J_{H,H}$ = 5.9, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.8 Hz, 2 H, H^5), 1.03 (s, $^2J_{Pt,H}$ = 74 Hz, 3 H, Pt-CH_3) ppm. **7:** $C_{17}H_{17}N_3O_3PtS$ (538.48): calcd. C 37.9, H 3.18, N 7.80; found C 38.1, H 3.20, N 7.78. ^{1}H NMR (CD_3NO_2): δ = 8.81 (d, $^3J_{H,H}$ = 5.9, $^3J_{Pt,H}$ = 51 Hz, 2 H, H^6), 8.53–8.25 (m, 7 H, H^4, H^3, H$^{3'}$, H$^{4'}$), 7.78 (ddd, $^3J_{H,H}$ = 5.9, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.8 Hz, 2 H, H^5), 1.03 (s, $^2J_{Pt,H}$ = 74 Hz, 3 H, Pt-CH_3), 2.47 (s, 3 H, CH_3SO_3) ppm. IR (nujol): $\tilde{\nu}$ = 1193, 1038 [$\nu(SO_3)$] cm^{-1}.

[Pt(OH)(terpy)](PF_6) (8): This complex was prepared according to a procedure reported for the analogous perchlorate salt[27] but with KPF_6 instead of $NaClO_4$ as the precipitating salt. Yield: 95%. $C_{15}H_{12}F_6N_3OPPt$ (590.32): calcd. C 30.5, H 2.05, N 7.12; found C 30.3, H 2.04, N 7.15. IR (nujol): $\tilde{\nu}$ = 3631 [ν(OH)], 884 [$\nu(PF_6)$] cm^{-1}.

[Pt(OCH$_3$)(terpy)](PF_6) (9): The procedure of Aldridge et al.[29] was applied starting from [Pt(OH)(terpy)](PF_6) instead of the BF_4^- salt. Yield: 90%. $C_{16}H_{15}F_6N_3OPPt$ (605.35): calcd. C 31.8, H 2.33, N 6.95; found C 31.6, H 2.32, N 6.98.

[Pt(terpy)(H_2O)](ClO_4)$_2$ (10): ***Caution!*** *Perchlorate salts of metal complexes are potentially explosive and should be handled with care.* This complex was prepared by adding a slight excess of $HClO_4$ (23 μL of a 65% solution in H_2O) to a stirred solution of **3** (0.1 g, 0.18 mmol) in TFE (15 mL). After 1 h, the yellowish solution was concentrated under vacuum to about 3 mL, diethyl ether was added with stirring, and the pale-yellow precipitate that formed was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 75% (0.087 g). $C_{15}H_{13}Cl_2N_3O_9Pt$ (645.26): calcd. C 26.6, H 1.93, N 6.20; found C 26.7, H 1.90, N 6.18. ^{1}H NMR (CD_3NO_2): δ = 8.76 (d, $^3J_{H,H}$ = 5.6, $^3J_{Pt,H}$ = 29 Hz, 2 H, H^6), 8.61–8.35 (m, 7 H, H^4, H^3, H$^{3'}$, H$^{4'}$), 8.04 (ddd, $^3J_{H,H}$ = 5.6, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.6 Hz, 2 H, H^5) ppm.

[Pt$_2$(μ-OH)(terpy)$_2$](ClO_4)$_3$ (11): This species formed when the acidolysis of **3** with excess $HClO_4$ was conducted in water (30 mL) instead of TFE. In this case the reaction was much slower, and the mixture was refluxed for 2 h before most of the product had precipitated from the solution. This was concentrated to about 10 mL and the orange solid collected by filtration, washed with a little ice-cold water, and dried under vacuum over P_2O_5. Yield: 84% (0.089 g). $C_{30}H_{23}Cl_3N_6O_{13}Pt_2$ (1172.1): calcd. C 30.7, H 1.98, N 7.17; found C 30.5, H 2.00, N 7.20.

[Pt$_2$(μ-OH)(terpy)$_2$](PF_6)$_2$(CF_3SO_3) (12): $CH_3OSO_2CF_3$ (0.1 mL, 0.9 mmol) was added to a suspension of **9** (0.3 g, 0.5 mmol), dried at 100 °C under vacuum over P_2O_5 just prior to use, in CH_2Cl_2

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(15 mL) and the mixture stirred at room temperature for about 30 min. The orange solid was then collected by filtration, washed with diethyl ether, and immediately placed in a dessicator over P_2O_5. Yield: 95% (0.312 g). $C_{31}H_{23}F_{15}N_6O_4P_2Pt_2S$ (1312.7): calcd. C 28.4, H 1.77, N 6.40; found C 28.5, H 1.78, N 6.37. ^{1}H NMR (**11**, **12**; CD_3NO_2, 298 K): δ = 9.43 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H^6), 8.57 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, H$_4'$), 8.48–8.31 (m, 6 H, H^3, H$^{3'}$, H^4), 7.88 (ddd, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 6.0, $^4J_{H,H}$ = 2.0 Hz, 2 H, H^5) ppm. IR (nujol): $\tilde{\nu}$ = 1167, 1248, 1297 [ν(CF_3SO_3)], 848 [ν(PF_6)] cm^{-1}. Crystals of the compound, suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a saturated $CHCl_3$ solution.

[Pt(terpy)(CH_3CN)][(CF_3SO_3)$_2$] (13): The preparation of this complex has been reported by Field et al.,[30] but we preferred a different procedure. Thus, CF_3SO_3H (10 μL, 0.11 mmol) was added to a stirred solution of **4** (0.06 g, 0.10 mmol) in acetonitrile (15 mL) under argon. After 1 h of stirring, the volume of the solution was reduced to about 3 mL by warming at 40 °C under a stream of argon. After cooling to room temperature, diethyl ether (20 mL) was added to precipitate a pale-yellow solid, which was filtered, washed with diethyl ether, and dried under vacuum. Yield: 91% (0.070 g). $C_{19}H_{14}F_6N_4O_6PtS_2$ (767.54): calcd. C 29.7, H 1.84, N 7.30; found C 29.5, H 1.79, N 7.22. ^{1}H NMR (CD_3NO_2): δ = 8.86 (d, $^3J_{H,H}$ = 5.1, $^3J_{Pt,H}$ = 34 Hz, 2 H, H^6), 8.65–8.42 (m, 7 H, H^4, H^3, H$^{3'}$, H$^{4'}$), 7.98 (ddd, $^3J_{H,H}$ = 5.1, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.8 Hz, 2 H, H^5), 3.00 (s, $^4J_{Pt,H}$ = 9.0 Hz, 3 H, NCCH_3) ppm. IR (nujol): $\tilde{\nu}$ = 2330, 2307 [ν(CN)]; 1260, 1158, 1030 [ν(CF_3SO_3)] cm^{-1}.

Reactions of Complexes 2–7 with CH_3SO_3H: These reactions were conducted in dry TFE. In a typical experiment, 1.0 mmol of the complex was dissolved in TFE (15 mL), and a solution of the acid (1.0 mmol) in the same solvent (2 mL) was added with stirring. In general, the solution became colorless within a few minutes. After stirring at room temperature for 1 h, the solution was concentrated to about 3 mL under vacuum, and diethyl ether was added dropwise with stirring. The resulting precipitate was collected by filtration, washed with diethyl ether, and dried under vacuum.

[Pt(OSO_2CH_3)(terpy)][PF_6] (2′): Yield: 92% (0.615 g). $C_{16}H_{14}F_6N_3O_3PPtS$ (668.41): calcd. C 28.8, H 2.11, N 6.29; found C 28.9, H 2.07, N 6.39. IR (nujol): $\tilde{\nu}$ = 1275, 1150, 1100 [ν (OSO_2)], 848 [ν (PF_6)] cm^{-1}.

[Pt(OSO_2CH_3)(terpy)][ClO_4] (3′): Yield: 90% (0.561 g). $C_{16}H_{14}ClN_3O_7PtS$ (622.89): calcd. C 30.9, H 2.27, N 6.75; found C 30.7, H 2.41, N 6.84.

[Pt(OSO_2CH_3)(terpy)][CF_3SO_3] (4′): Yield: 87% (0.585 g). $C_{17}H_{14}F_3N_3O_6PtS_2$ (672.51): calcd. C 30.4, H 2.10, N 6.24; found C 30.2, H 2.22, N 6.28.

[Pt(OSO_2CH_3)(terpy)][BF_4] (5′): Yield: 88% (0.537 g). $C_{16}H_{14}BF_4N_3O_3PtS$ (610.25): calcd. C 31.5, H 2.31, N 6.89; found C 31.6, H 2.44, N 6.82. ^{1}H NMR (**2′**, **3′**, **4′**, **5′**; CD_3NO_2): δ = 8.86 (d, $^3J_{H,H}$ = 5.6, $^3J_{Pt,H}$ = 32 Hz, 2 H, H^6), 8.59–8.34 (m, 7 H, H^4, H^3, H$^{3'}$, H$^{4'}$), 7.98 (ddd, $^3J_{H,H}$ = 5.6, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 2.0 Hz, 2 H, H^5), 3.11 (s, 3 H, SO_3CH_3) ppm.

[Pt(OSO_2CH_3)(terpy)][Pt(ONO_2)(terpy)][(CH_3SO_3)(NO_3) (6′): Yield: 85% (0.498 g). $C_{16}H_{14}N_4O_6PtS$ (585.45): calcd. C 32.8, H 2.41, N 9.57; found C 32.6, H 2.47, N 9.62. ^{1}H NMR (CD_3NO_2): δ = 8.87 (d, $^3J_{H,H}$ = 6.5, $^3J_{Pt,H}$ = 32 Hz, 2 H, H^6), 8.58 (d, $^3J_{H,H}$ = 6.0, $^3J_{Pt,H}$ = 27 Hz, 2 H, H^6), 8.59–8.31 (m, 14 H, H^4, H^3, H$^{3'}$, H$^{4'}$), 7.98 (m, 4 H, H^5), 3.11 (s, 3 H, $PtSO_3CH_3$), 2.47 (s, 3 H, SO_3CH_3) ppm. IR (nujol): $\tilde{\nu}$ = 1519 [ν(ONO_2)], 1360 [ν(NO_3)], 1275, 1150 [ν(OSO_2)], 1203, 1045 [ν (SO_3)] cm^{-1}.

[Pt(OSO_2CH_3)(terpy)][(CH_3SO_3) (7′): Yield: 87% (0.538 g). $C_{17}H_{17}N_3O_6PtS_2$ (618.54): calcd. C 33.0, H 2.77, N 6.79; found C 33.2, H 2.64, N 6.92. ^{1}H NMR (CD_3NO_2): δ = 8.86 (d, $^3J_{H,H}$ = 5.6, $^3J_{Pt,H}$ = 32 Hz, 2 H, H^6), 8.59–8.34 (m, 7 H, H^4, H^3, H$^{3'}$, H$^{4'}$), 7.98 (ddd, $^3J_{H,H}$ = 5.6, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 2.0 Hz, 2 H, H^5), 3.11 (s, 3 H, SO_3CH_3), 2.47 (s, 3 H, SO_3CH_3) ppm.

[Pt(terpy)(H_2O)][(CF_3SO_3)$_2$] (8′). Method (a): CF_3SO_3H (10 μL, 0.11 mmol) was added with a microsyringe fitted with a teflon needle to a stirred solution of **4** (0.06 g, 0.10 mmol) in freshly distilled TFE (10 mL) under dry argon. The color of the solution immediately turned from orange to pale yellow. After stirring for 30 min, diethyl ether (20 mL) was added, and the resulting yellow-orange precipitate was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 91% (0.068 g). **Method (b):** All operations were performed under dry nitrogen with the aid of a glove box.

Table 1. Crystal data and details of data collection and refinement procedure for complexes **8′** and **12**.

	8′	**12**
Empirical formula	$(C_{15}H_{11}N_3)(H_2O)Pt{\cdot}2(CF_3SO_3)$	$(C_{30}H_{22}N_6)(OH)Pt_2{\cdot}CF_3SO_3{\cdot}2(PF_6)$
Formula mass	744.51	1312.73
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/a$
a [Å]	8.6885(2)	9.4928(1)
b [Å]	28.5640(7)	36.6228(5)
c [Å]	9.4721(2)	10.9921(1)
β [°]	104.460(1)	91.5753(3)
V [Å^3]	2276.30(9)	3819.99(7)
Z	4	4
$D_{calcd.}$ [g cm^{-3}]	2.172	2.283
T [K]	295	295
μ [cm^{-1}]	64.43	75.75
θ_{min}–θ_{max} [°]	2.3–28.0	2.8–28.0
Unique reflections	5392	8910
R_{int}	0.070	0.059
Observed reflections [$I > 2\sigma(I)$]	4542	6770
R (observed reflections)	0.0382	0.0516
wR (all reflections)	0.0904	0.1359
S	1.106	1.061
Largest $\Delta F_{max/min}$ [e Å^{-3}]	0.58/–1.39	1.84/–1.40

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The acid (10 μL, 0.11 mmol) was added to a stirred suspension of **4** (0.06 g, 0.10 mmol) in dry CH_2Cl_2 (5 mL), and stirring was continued for about 15 min. The solid was then filtered, washed carefully with diethyl ether, and dried under vacuum. Yield: 91% (0.068 g). $C_{17}H_{13}F_6N_3O_7PtS_2$ (744.50): calcd. C 27.4, H 1.76, N 5.64; found (a) C 27.0, H 1.92, N 5.69; (b) C 27.1, H 1.83, N 5.72. ^{1}H NMR (CD_3NO_2): δ = 8.76, 8.67 (2 d, 2 H, first d with $^3J_{H,H}$ = 5.6 Hz, second d with $^3J_{H,H}$ = 5.6 Hz, H^6), 8.61–8.35 (m, 7 H, H^4, H^3, $H^{3'}$, $H^{4'}$), 8.04 (ddd, $^3J_{H,H}$ = 5.6, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.6 Hz, 2 H, H^5) ppm. IR (nujol): $\tilde{\nu}$ = 1166, 1235, 1290 [$\nu(CF_3SO_3)$] cm^{-1}. Slow concentration of a chloroform solution of the product gave orange crystals suitable for X-ray crystal structure determination.

X-ray Structure Determination: Crystal data for compounds **8′** and **12** were collected using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation. The data sets were integrated with the Denzo-SMN package[31] and corrected for Lorentz, polarization, and absorption (SORTAV[32]) effects. The structures were solved by direct methods (SIR97[33]). The structure of **8′** was refined using full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic. The non-hydrogen atoms of the dimeric $[Pt_2(\mu\text{-}OH)(terpy)_2]^{3+}$ complex cation and the PF_6^- anion in the structure **12** were refined anisotropically. The other PF_6^- anion as well as the triflate anion were found to be disordered. The fluorine and oxygen atoms of these groups were refined isotropically over two positions with an occupancy of 0.5 each; the P, C, and S atoms were refined anisotropically. All calculations were performed using SHELXL-97[34] and PARST,[35] as implemented in the WINGX[36] system of programs. The crystal data and refinement parameters are summarized in Table 1. Selected interatomic distances and angles are given in Tables 2 and 3 for compounds **8′** and **12**, respectively. CCDC-654357 and -654358 (for complexes **8′** and **12**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Selected bond lengths [Å] and angles [°] for complex **8′**.

Distances			
Pt1–O1	2.040(5)	Pt1–N2	1.914(4)
Pt1–N1	2.021(5)	Pt1–N3	2.009(4)
Angles			
O1–Pt1–N1	101.5(2)	N1–Pt1–N2	81.4(2)
O1–Pt1–N2	176.6(6)	N1–Pt1–N3	163.3(2)
O1–Pt1–N3	95.2(2)	N2–Pt1–N3	81.8(2)
Hydrogen bonds			
O1–H10	0.93(9)	O1–H20	0.73(7)
O1···O3	2.650(8)	O1···O7	2.617(10)
H10···O3	1.74(9)	H20···O7	1.91(7)
O1–H10···O3	165(8)	O1–H20···O7	163(7)

Table 3. Selected bond lengths [Å] and angles [°] for complex **12**.

Distances			
Pt1–O1	2.033(6)	Pt2–O1	2.024(6)
Pt1–N1	2.019(7)	Pt2–N4	2.022(7)
Pt1–N2	1.906(7)	Pt2–N5	1.917(6)
Pt1–N3	2.016(7)	Pt2–N6	2.036(7)
Angles			
O1–Pt1–N1	98.8(3)	O1–Pt2–N4	97.7(3)
O1–Pt1–N2	176.3(3)	O1–Pt2–N5	176.8(2)
O1–Pt1–N3	97.7(3)	O1–Pt2–N6	99.7(3)
N1–Pt1–N2	82.1(3)	N4–Pt2–N5	81.6(3)
N1–Pt1–N3	163.5(3)	N4–Pt2–N6	162.6(3)
N2–Pt1–N3	81.4(3)	N5–Pt2–N6	81.0(3)
Pt1–O1–Pt2	138.2(3)		
Hydrogen bonds			
O1–H100	0.93		
O1···O2	2.056(15)		
H100···O2	1.83		
O1–H100···O2	146		

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